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SEMI-METAL CLUSTERS: LASER VAPORIZATION AND
PHOTOIONIZATIONAL OF ANTIMONY AND BISMUTH(U) GEORGIA
UNIV ATHENS DEPT OF CHEMISTRY R G WHEELER ET AL

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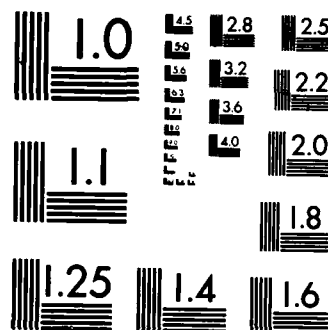
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SEMI-METAL CLUSTERS: LASER VAPORIZATION AND PHOTOIONIZATION
OF ANTIMONY AND BISMUTH

by

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Abstract

Gas phase metal clusters of antimony, bismuth, or antimony bismuth alloys are prepared by laser vaporization and probed with UV laser photoionization in a time-of-flight mass spectrometer. Unusual size distributions are observed, ending at five atom clusters. Fragmentation processes are extremely efficient at 193 nm for tetramer species regardless of elemental composition. Striking similarities in cluster stability and fragmentation patterns in these systems suggest that bonding is dominated by contributions from valence s and p electrons.

Introduction

The study of gas phase metal dimers and larger metal clusters has become increasingly popular since the introduction of laser vaporization techniques for cluster production in molecular beams¹ and laser photoionization mass spectroscopy^{1a,2} for sensitive cluster detection. Transition metals have been the main objects of interest for rovibronic spectroscopy of dimers³ and trimers⁴⁻⁶ as well as for size dependent studies of ionization potentials,⁷ magnetic properties,⁸ reactivity,⁹ and ion fragmentation.¹⁰ Additionally, gas phase clusters of semiconductor and insulator materials have also been investigated to probe electronic structure and reactivity.¹¹⁻¹³ Based on solid state properties, post transition metals (Sn, Bi, Pb, Sb, etc.) might be expected to form cluster species with properties intermediate between those of transition metals or semiconductors and insulators. Clusters of these lower melting materials have in fact been produced and characterized in oven/beam experiments using inert gas condensation techniques and electron impact ionization mass spectroscopy.^{14,15} Interestingly, these experiments suggest a rich variety of cluster properties with cluster size distributions characterized by striking patterns of "magic numbers." However, mass spectral abundances in these experiments are often difficult to interpret because of fragmentation processes in electron impact ionization.¹⁶ For an alternative probe of magic number patterns in these systems, we have initiated experiments using laser vaporization for cluster production and UV laser photoionization for detection. In this letter we present our initial results for antimony and bismuth clusters, as well as for antimony-bismuth alloy clusters.

Due to their characteristic bulk conductivity and crystal lattice properties antimony and bismuth are commonly referred to as semi-metals. The equilibrium vapors of these materials contain diatomic and tetratomic molecular species, and have been studied extensively with mass spectroscopy yielding electron impact appearance potentials and thermodynamic properties.¹⁷⁻¹⁹ In oven/beam experiments using inert gas condensation techniques clusters of up to 150-200 atoms have been produced.¹⁴ In the case of antimony, these large clusters are composed of tetramer building

blocks, and magic numbers in mass spectral abundances have been rationalized in terms of stable packing arrangements of tetrahedral units.^{14c}

In striking contrast to oven beam experiments, our laser vaporization source produces no clusters larger than five atoms. The complete absence of larger clusters in our experiment can be understood in terms of the different source conditions and the stability of the clusters produced. Fortunately, the limited size range of clusters formed makes it convenient to study photoionization and fragmentation in these cluster systems. Surprisingly, both cluster growth and ion fragmentation processes are virtually identical for antimony, bismuth, and mixed antimony-bismuth clusters. This suggests that bonding in these systems is dominated by valence shell s and p electrons without substantial participation of underlying d or f shells.

Experimental Details

The laser vaporization source used in these experiments is essentially the same as that used in previous studies of metal clusters.² We use a double solenoid type pulsed nozzle (Newport Corporation BV-100V) operating with 6 atm backing pressure of helium, 1 mm orifice diameter, 200 μ s pulse duration, and 10-20 Hz repetition rate. Vaporization is accomplished by a focused (\sim 1 mm spot) excimer laser (Lumonics 861-M-4) operating at either 193 or 249 nm. Samples are prepared by melting pellets of either the pure metals or a desired mixture into a test-tube mold to produce a $\frac{1}{2}$ inch diameter rod. Vaporization occurs within a housing attached to the nozzle face-plate where the pulsed helium flow is confined to a 2 mm diameter channel over the sample rod surface. Following the vaporization laser pulse, collisional energy transfer with helium cools the metal vapor and clusters grow in the channel extending beyond the vaporization point (also 2 mm diameter). The length of the growth region can be varied from 5 mm to 50 mm by addition of modular channel segments.

The metal cluster/helium mixture expands freely out of the pulsed source into a vacuum system described previously,²⁰ where it is collimated into a beam by a downstream skimmer before entering the

differentially-pumped detection chamber. Photoionization is accomplished by a second excimer laser crossing the molecular beam in the source region of a homemade time-of-flight mass spectrometer. Positive ion mass spectra are processed with a Camac-based 100 MHz transient digitizer connected to an averaging memory module (Transiac 2101 system) under computer control (DEC PRO-350 computer via an IEEE-488 bus and Lecroy 8901A Camac crate controller).

Results and Discussion

The mass spectra obtained for laser vaporization of antimony, bismuth, and a 1:1 molar BiSb alloy, with photoionization at 193 and 157 nm, are shown in Figures 1-3. Several aspects of these spectra are noteworthy and are discussed in detail below. First of all, each spectrum contains cluster species up to only five atoms in size. Secondly, mass spectral intensities in each system are extremely wavelength dependent. Finally, tetramer species in each cluster system are missing, or nearly missing, in 193 nm spectra, but are observed with significant abundance in corresponding 157 nm spectra.

An abruptly truncated cluster distribution like that observed here has not been reported previously. We have therefore conducted extensive tests to determine that this is a fundamental property of these cluster elements rather than a limitation of metal vapor density in our source or a result of fragmentation in photoionization detection. For comparison, the same nozzle source used here has produced clusters of 30-40 atoms of lead or tin, and 15-20 atom clusters of higher melting metals such as nickel in other experiments in our lab. The amount of material removed from sample rods by vaporization is roughly the same here as in these other experiments. Additionally, species containing more than five atoms of antimony or bismuth are produced by vaporization of SnBi or PbSb alloys, and detected with photoionization at these wavelengths, but only when at least one atom of the other element is present in the cluster. Metal clusters produced in laser sources are believed to grow by sequential atom addition. Although we cannot rule out some direct vaporization of molecular species, our mass spectral data do show substantial concentrations

of atoms available for cluster growth. The time or number of collisions for growth to occur are controlled by the length of the nozzle channel downstream from the vaporization point. Adjustment of this channel length between 0.5 and 4.5 cm (in 1.0 cm increments) does not affect the observed cluster distribution. Photoionization detection conditions have also been varied to check for fragmentation. Two laser wavelengths (193 and 157 nm) were used for ionization, over a broad range of laser powers (193 nm: 10.0-0.1 mJ/cm²; 157 nm: 1.0-0.06 mJ/cm²), without ever detecting any clusters larger than five atoms. Although multiphoton ionization at 565 nm has been observed to cause extensive fragmentation for bismuth clusters¹⁴, complete fragmentation for near threshold photoionization at two different UV wavelengths is extremely unlikely. We have now reproduced these data in approximately 10 different experiments on different days and conclude that clusters larger than five atoms of these pure elements are not produced by our source.

The fact that larger clusters are not produced when there is a sufficient density of metal vapor implies either some activation barrier to cluster growth or that clusters beyond five atoms form initially but decompose because of instability. We know of no mechanism to explain an activation barrier to cluster growth by single atom addition. Therefore, we conclude that it is the instability of clusters just beyond five atoms (i.e. 6 or 7) with respect to atom loss that limits the observation of larger clusters.

Since larger clusters of these same metals are formed in oven/beam experiments, it is important to examine the dynamics of cluster growth in our source for comparison. Smalley and coworkers have analyzed the gas dynamics in nozzle sources in detail, and our conditions are similar to theirs.²¹ Our measured throughput and time characteristics indicate a helium pressure of approximately one atmosphere in the source channel during cluster growth. A typical cluster molecule, then, experiences 10⁴-10⁵ collisions with helium while traversing this region. At this collision rate, the superheated metal initially vaporized is rapidly quenched to the nozzle wall temperature and cluster growth in the channel occurs at or very near room temperature (300°K). At the end of the growth zone, the mixture of helium and metal vapor expands supersonically into

the vacuum. In this expansion weakly bound van der Waals complexes may form if there is sufficient metal vapor density. Density is reduced along the growth channel, however, by deposition on the walls. The invariance in cluster size with channel length, which affects the density of metal expanded as a free jet, indicates that growth occurs inside the channel, at room temperature, rather than in the expansion exiting the channel. This is in contrast to cluster growth in oven/beam experiments where densities are greater and growth can occur at cold temperatures in expansions out of the metal oven.

If larger clusters are not stable under room temperature growth conditions in our source, it is possible to estimate upper and lower limits for binding energies using absolute rate theory.²² Under typical operating conditions the residence time of clusters in the growth channel is 50 μ s. Using pre-exponential factors between 10^{12} and 10^{13} $\text{cm}^3/\text{mol}\cdot\text{sec}$, and allowing for small deviations from complete thermalization, we obtain a characteristic binding energy for our source of 11 ± 2 kcal/mole. Therefore, cluster species observed from this source must be bound with respect to atom loss by more than 11 kcal/mole while clusters not observed are bound by less than this value. Our findings are in agreement with mass spectral thermodynamic data for these elements where comparison is possible.¹⁷⁻¹⁹ For antimony and bismuth, we can only apply this reasoning up to the 6 and possibly the 7 atom cluster with good confidence. Larger clusters may be more stable, but could not grow beyond the 6 or 7 atom "bottleneck" by single atom addition.²⁵ Aggregation of tetramer units has been observed in oven/beam experiments but is not observed in our data. This could imply that tetramer-tetramer bonding is weak, or it may be that the density of tetramers in our source is too low for aggregation.

Another interesting feature of these cluster systems is the laser wavelength and power dependences of mass spectral abundances. At 193 nm, relative intensities across the spectra change dramatically with laser power and intensity dependences are non-linear down to the threshold for ion detection ($0.1 \text{ mJ}/\text{cm}^2$). This indicates that at least two-photons are required for photoionization and that ion fragmentation processes are efficient. At 157 nm, fragmentation is also efficient at higher power

(1.0 mJ/cm²), but some peaks have linear power dependences and constant relative intensities in the limit of low power (< 0.1 mJ/cm²). These studies establish upper and lower limits on ionization thresholds which are compared to previous electron impact data in Table I.

Perhaps the most interesting aspect of mass spectral intensities is the virtual absence of tetramer mass peaks in spectra at 193 nm. This behavior is observed for both antimony and bismuth clusters down to the threshold for ion detection. This is a surprising result since equilibrium mass spectral studies find the tetramer to be especially abundant and stable. Based on EI appearance potentials¹⁷⁻¹⁹ ionization at 193 nm requires two photons, depositing about 5 eV of excess energy into tetramer ions and so fragmentation in this channel is not unexpected. At 157 nm, near threshold single photon ionization is possible and tetramer species are observed without serious fragmentation. The BiSb mixed clusters show this same behavior in a dramatic way: all possible 4 atom clusters (0,4; 1,3; 3,1; 2,2, 4,0 in Figure 3) are missing in the 193 nm spectrum while the 157 nm spectrum shows that they are all present as neutrals in the molecular beam.

It is significant that cluster stability and tetramer fragmentation processes in these systems are so unusual and so similar for antimony, bismuth, and all possible mixed clusters of these elements. The component Sb and Bi atoms are of course isoelectronic in the valence shell but they differ substantially in the underlying electron configurations (4d versus 5d and 4f). That properties dependent on electronic structure are independent of elemental identity suggests that bonding in these systems is dominated by valence shell s and p electrons. This kind of bonding is quite different from that observed in transition metals, but is consistent with the success of simple electron counting schemes used to describe post transition metal ionic clusters in condensed phases (so called Zintl ions).^{23,24} A correspondence between electronic structure for condensed phase clusters and that of gas phase clusters has interesting implications for the expected stability and structure of other post transition element systems. Experiments on these systems are now in progress in our laboratory.

Conclusion

Gas phase metal and mixed clusters of the post transition elements antimony and bismuth have been prepared by laser vaporization techniques and studied by laser photoionization mass spectroscopy. These systems are characterized by unusual cluster size distributions, ending sharply at five atoms, and by extremely efficient fragmentation processes in all tetramer species at 193 nm. These data suggest that post transition element clusters in general may have interesting electronic structure properties intermediate between those of transition metals and semiconductors or insulators.

Acknowledgment

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25. These conclusions also do not apply to ionic clusters of these metals. Sb_x and Bi_x positive ions ($x = 6-10$) are observed in the fragmentation of Bi/Sn and Pb/Sb alloy clusters (our results to be published). Bi_x cations ($x = 1-13$) are also observed by direct sampling of the plasma from a laser vaporization source (M. E. Geusic, R. R. Freeman, and coworkers, to be published).

Figure Captions

Figure 1 - Time-of-flight mass spectra obtained for antimony clusters at 193 nm (laser power - 10 mJ/cm²) and 157 nm (laser power 1.0 mJ/cm²). Unlabeled peaks are due to small concentrations of oxides. Spectra were accumulated as an average of 500 laser shots. As in all photoionization data, peak intensities represent the combined effects of neutral cluster density, ionization potentials and cross sections, and fragmentation patterns. Upper and lower traces are not normalized to the same absolute intensity scale.

Figure 2 - Time-of-flight mass spectra obtained for bismuth clusters under the same conditions of Figure 1.

Figure 3 - Time-of-flight mass spectra obtained for 1:1 molar bismuth-antimony alloy clusters. All peaks including smaller unlabeled ones are assigned to mixed cluster species containing five or less atoms.

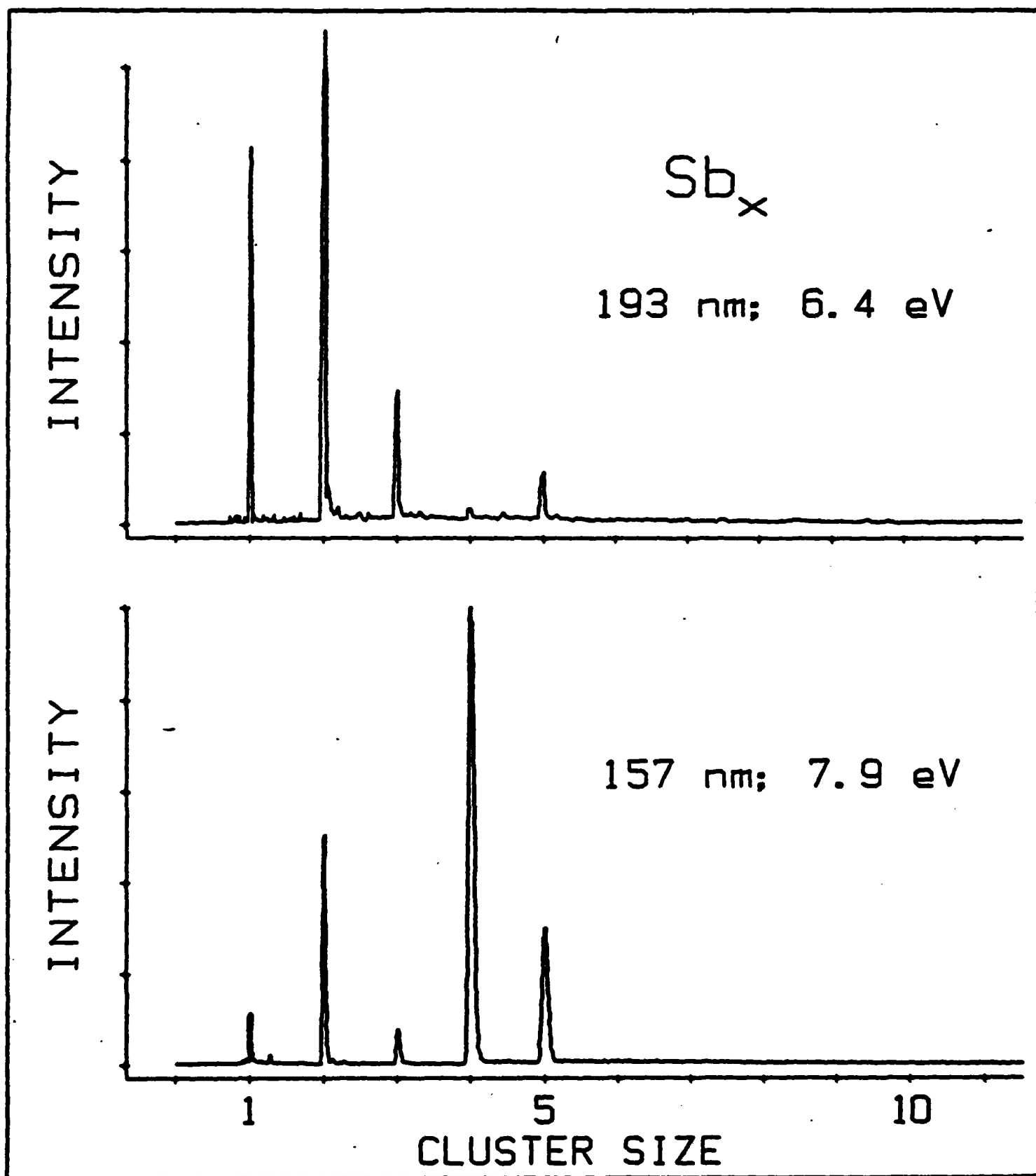


FIGURE 1

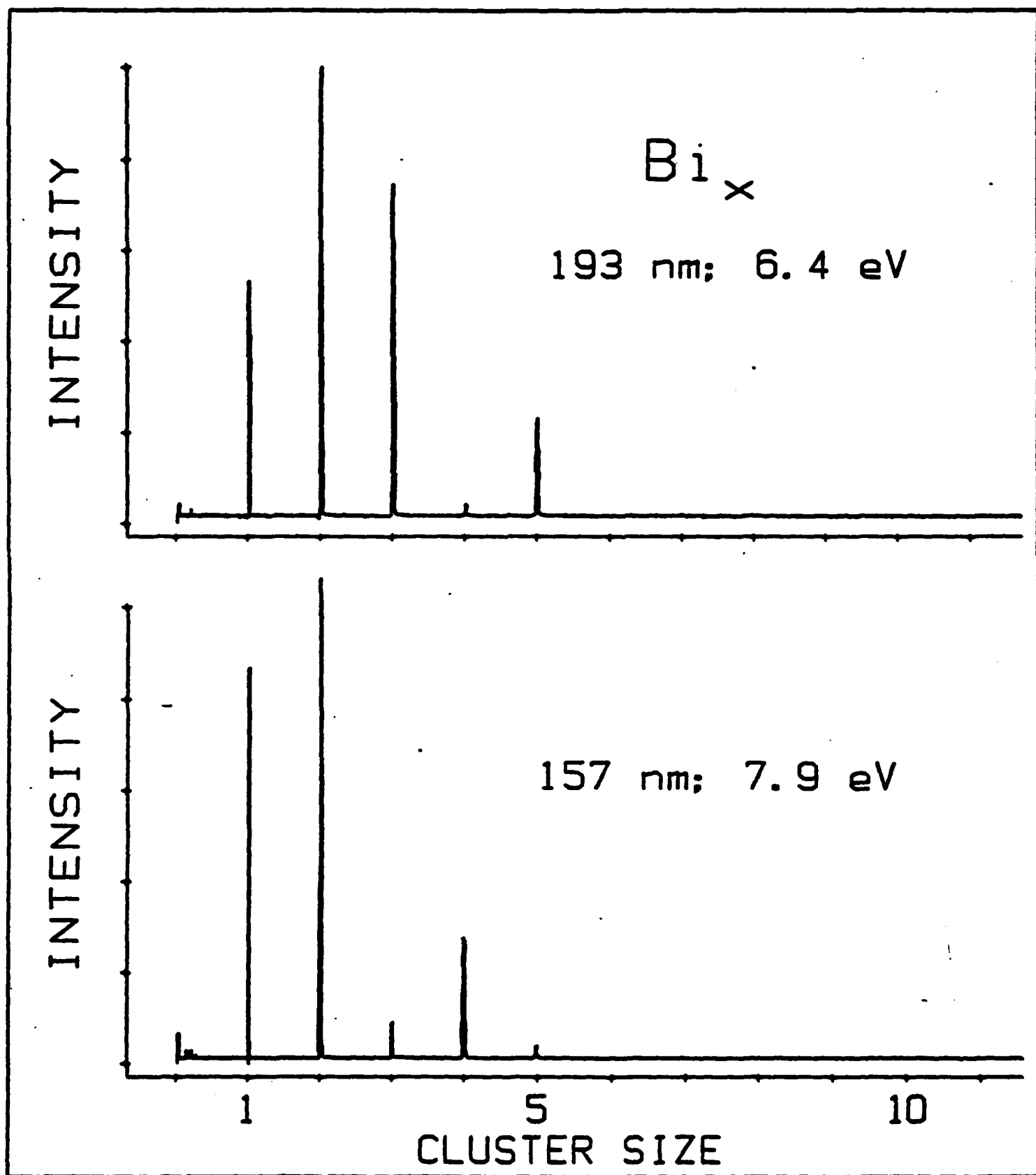


FIGURE 2

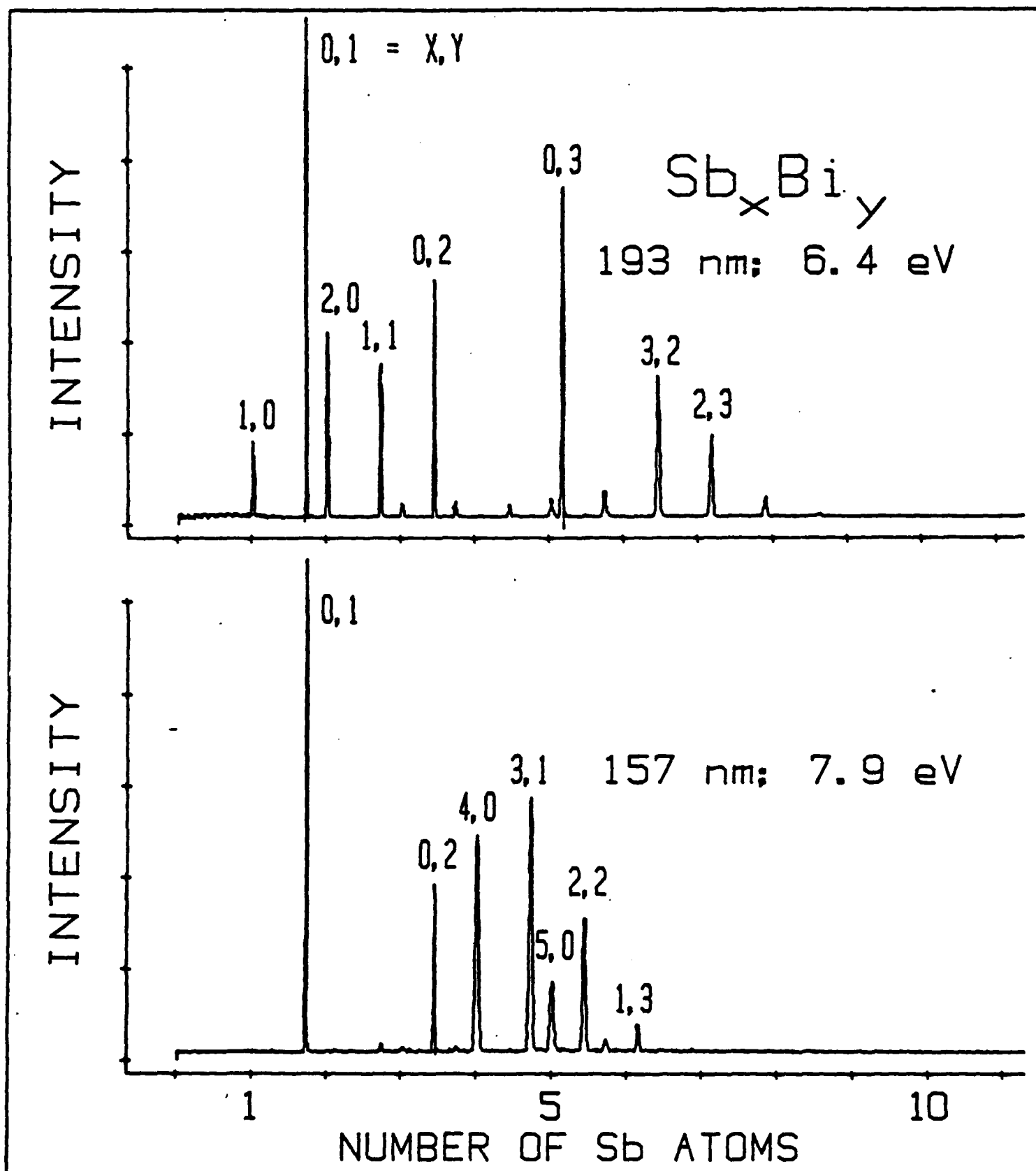


FIGURE 3

Table I. Antimony and bismuth appearance potentials. Units are electron volts (eV).

<u>This work (PI)</u> -		<u>Literature (EI)</u>
Sb	> 7.9	8.64
Sb ₂	> 7.9	8.7(1), 8.4(2)
Sb ₃	> 7.9	10.4(1)
Sb ₄	6.4 < AP < 7.9	8.3(1), 7.7(2)
Sb ₅	6.4 < AP < 7.9	
Bi	6.4 < AP < 7.9	7.29
Bi ₂	6.4 < AP < 7.9	7.5(1), 8.0(2)
Bi ₃	> 7.9	
Bi ₄	6.4 < AP < 7.9	7.6(1)
Bi ₅	6.4 < AP < 7.9	

1) Reference 18.

2) Reference 17.

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